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# A Matlab-IPhreeqc based model integrating mass transfer, microbial dynamics, contaminant degradation, and geochemistry to interpret biological assays: An example for PCE dechlorination

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**Introduction**

Organohalide respiration (OHR) of chlorinated ethenes is a key process naturally occurring in contaminated groundwater and used in engineered bioremediation technologies. Under reducing conditions, bacteria capable of OHR (OHRB) use toxic chlorinated ethenes such as perchloroethene (PCE) as an electron acceptor and sequentially degrade it to trichoroethene (TCE), *cis*-dichloroethene (cDCE), vinyl chloride (VC) and ultimately to a non-toxic endpoint, ethene. Despite the extensive investigation of this degradation process, natural attenuation and enhanced bioremediation efforts still sometimes stall before the harmless endpoint is reached.

Evidence shows that other members of the groundwater microbial community, such as iron- or sulfate-reducing bacteria (FeRB, SRB), may cause or contribute to this stall [1]. A combination of modeling and laboratory experiments were used to investigate the effects of competing respiration processes on OHR of chlorinated ethenes.

**Experimental Setup**

Batch experiments used to explore the dynamics of a microbial community containing OHRB were carried out in anaerobic conditions in 125-mL serum bottles sealed with butyl rubber stoppers. The experimental system consisted of three phases – an aqueous phase containing the culture medium, a gaseous phase containing $CO_2$ and electron donor $H_2$, and an organic phase of hexadecane and PCE. Because of the high hexadecane-water partition coefficient of PCE [2], the organic phase acts as a source and allows the batch concentration of PCE to remain high while the aqueous concentration remains at levels that are non-toxic to the bacteria.

An OHRB consortium containing *Sulfurospirillum diekertiae* [3] that is capable of degrading PCE to TCE was used in conjunction with FeRB *Shewanella oneidensis* and SRB *Desulfovibrio vulgaris*. Ferric citrate and sodium sulfate were given as electron acceptors for the FeRB and SRB, and $H_2$ was supplied in excess as the only electron donor for all three guilds. Samples were taken periodically over a span of four days and were analyzed for aqueous chloride using a chlor-o-counter instrument, iron(II) using a colorimetric ferrozine method, sulfate using ion chromatography, and community composition using terminal restriction fragment length polymorphism.

**Modeling Approach and Application**

In order to quantitatively understand how the microbial community dynamics impact chlorinated ethene degradation, it is essential to account for mass transfer of electron donor/acceptor between the phases and iron and sulfate geochemistry as well as degradation kinetics. Determination of Michaelis-Menten kinetic parameters, such as the maximum specific degradation rate and half-velocity constant, was accomplished by accounting for the effect mass transfer on the aqueous concentration [4]. Similarly, chemical reduction of iron(III) by sulfide produced during sulfate respiration by SRB must be accounted for to accurately determine the extent of iron(III)-respiration by FeRB.

Sample removal and its effect on phase volume and thus mass transfer is also included [5]. Figure 1 depicts a conceptual model of the system. The integrated modeling approach proposed in this study is based on a Matlab-IPhreeqc coupling. In the model, mass removal and interphase mass transfer processes are executed in Matlab, whereas chemical reactions and microbial kinetics are executed using the geochemical code PHREEQC [6]. An operator-split approach and the IPhreeqc module [7] are used to couple the two codes.

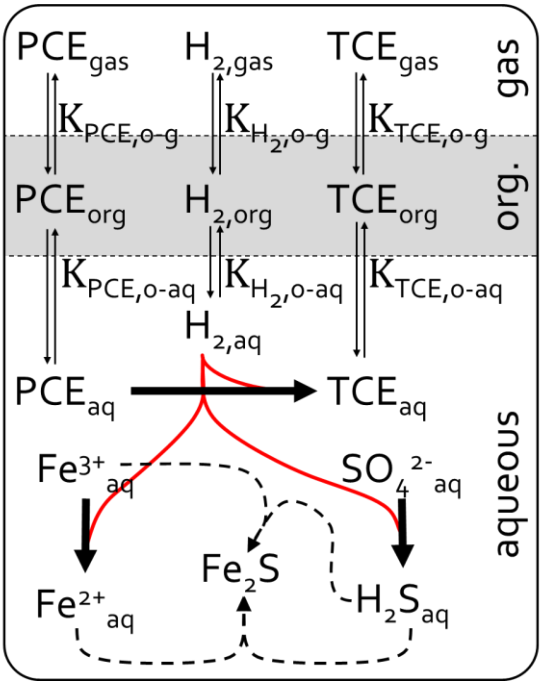


*Figure 1:* Conceptual model – *K* indicates mass transfer rates, all other variables indicate concentrations, bold arrows indicate microbial respiration processes, red lines indicate processes using hydrogen, and dashed lines indicate geochemical processes included in the model.

The proposed modeling approach has been applied to simulate the experiments performed in this study and has vitally aided in quantifying PCE dechlorination and the specific contribution of each physical, chemical and biological process to the complex system that occurs in the three-phase experimental setup.

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